

MECHANISM OF THE INTERACTION BETWEEN TWO
REDOX OXIDES IN GLASS

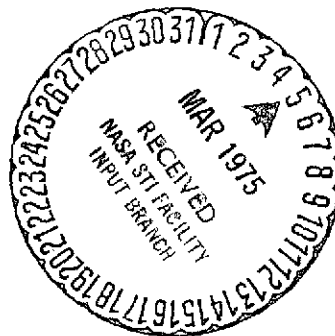
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(NASA-TT-F-16198) MECHANISM OF THE
INTERACTION BETWEEN TWO REDOX OXIDES IN
GLASS (Scientific Translation Service) 19 p
HC \$3.25 CSCL 11B

N75-17509

Unclas
G3/27 10248

Translation of "Mechanismus der Wechsel-
wirkung zweier Redox-Oxide in Glas",
Glastechnische Berichte, Vol. 47, Part 1,
January 1974, pp. 4 - 9.



1. Report No. NASA TT F-16,198		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Mechanism of the interaction between two redox oxides in glass				5. Report Date February 1975	
				6. Performing Organization Code	
7. Author(s) D. Lahiri, B. Mukherjee and R. N. Majumdar				8. Performing Organization Report No.	
				10. Work Unit No.	
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108				11. Contract or Grant No. NASw-2483	
				13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Mechanismus der Wechselwirkung zweier Redox-Oxide in Glas", Glastechnische Berichte, Vol. 47, Part 1, January 1974, pp. 4 - 9.					
16. Abstract Density and viscosity measurements on the glasses $\text{Na}_2\text{O} \cdot x \text{MeO} \cdot (6 - x) \text{SiO}_2$ were carried out both at high and low temperatures. The molar volume and the viscosity data show the magnesium ions in the glass systems studied occur in tetrahedral and octahedral configurations at low and high temperatures respectively.					
17. Key Words (Selected by Author(s))				18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 18	
				22. Price	

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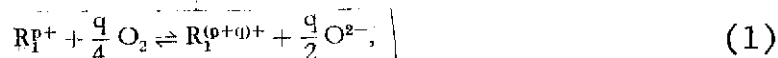
Durgadas Lahiri, Balai Mukherjee and Rabindra Nath Majumdar

When a glass is melted with a redox oxide, there is a distribution between the two oxidation states, with the proportions changing, depending on the atmosphere, until equilibrium is attained.

If the glass contains more than one redox oxide, then in general a type of reciprocal interaction occurs between the redox pairs. One oxide acts as the oxidant for the other. Kühl et al. [1] arranged the redox pairs in a series so that an oxide in a glass is oxidized by one above it in the series. Paul and Douglas [2] found no indication which could explain this reciprocal action in glasses with different redox pairs having complex formation or association. They suggested a mechanism for the mutual interaction between the redox pairs. Another possible mechanism is suggested in this work.

1. Calculation of the Equilibrium Constants

Suppose that a glass contains an oxide which can exist in two oxidation states, R^{p+} and R^{p+q+} . The glass is brought to equilibrium with air at the melt temperature and also at room temperature. If the equilibrium constants at these two temperatures are K_1 and K_2 , and we have

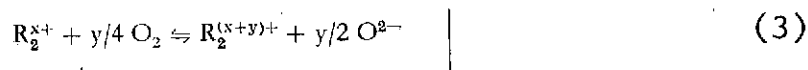


*Translator's Note: Numbers in margin indicate pagination of original foreign text.

for the reaction, then for K_1 or K_2 we have

$$\frac{[R_1^{(p+q)+}] \cdot [O^{2-}]^{q/2}}{[R_1^{p+}] \cdot [O_2]^{q/4}} \quad (2)$$

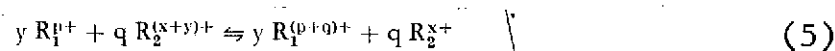
If this glass contains the same composition of another oxide, R_2 , which can exist in the states R_2^{x+} and $R_2^{(x+y)+}$, and if it is also brought to equilibrium with air at the melt temperature and at room temperature, then for the reaction



we can give the constants K_3 or K_4 for the reaction as

$$K_3 \text{ or } K_4 = \frac{[R_2^{(x+y)+}] \cdot [O^{2-}]^{y/2}}{[R_2^{x+}] \cdot [O_2]^{y/4}} \quad (4)$$

In glasses with both redox oxides, equations (2) and (4) can be combined to



with

$$K = \frac{(K_1)^y}{(K_3)^q} \text{ or } \frac{(K_2)^y}{(K_4)^q} = \frac{[R_1^{(p+q)+}]^y}{[R_1^{p+}]^y} \times \frac{[R_2^{x+}]^q}{[R_2^{(x+y)+}]^q} \quad (6)$$

Here we must note that the rate constant for the total reaction, K , by which the glass is brought to equilibrium in air ($P_{O_2} = 0.21 \text{ atm}$) is independent of the oxygen partial pressure, although it can be calculated. It depends only on the temperature.

Equation (6) states the relative proportions of R_1^{p+} , $R_1^{(p+q)+}$, R_2^{x+} , and $R_2^{(x+y)+}$ which exist in equilibrium at the melt temperature or at room temperature. It is obvious that

$$\frac{(K_1)^y}{(K_3)^q} > \frac{(K_2)^y}{(K_4)^q}$$

and especially for the case

$$\frac{(K_4)^q}{(K_3)^q} > \frac{(K_2)^y}{(K_1)^y}$$

the concentrations of $R_1^{(p+q)+}$ and R_2^{x+} decrease on cooling to room temperature, while those of $R_2^{(x+y)+}$ and R_1^{p+} increase, if the melt contains both R_1 and R_2 , and if it is brought to equilibrium in air at the melt temperature, and if it is assumed that no oxygen is present for reactions (1) and (2) on cooling. This assumption is reasonable, because a glass melt contains very little dissolved oxygen and the time for cooling of the melt is too brief for the necessary oxygen to be able to diffuse from the atmosphere into the melt. Such an assumption is made in all studies of redox equilibria in glass. If, on the other hand, equilibration with atmospheric oxygen occurs during cooling, the proportions of $R_1^{(p+q)+}$ and R_1^{p+} are determined by the value of K_2 , and the proportions of R_2^{x+} and $R_2^{(x+y)+}$ are determined by the value of K_4 , independent of whether the two redox oxides are separated in two glasses or if they occur together in one glass.

The concentration changes of the different redox oxides on cooling from the melt temperature to room temperature can be calculated using Equation (6). For the equilibrium constant, K , of the total reaction at room temperature we get:

$$K = \frac{(K_2)^y}{(K_4)^q} = \frac{[R_1^{(p+q)+}]^y \cdot [R_2^{x+}]^q}{[R_1^{p+}]^y \cdot [R_2^{(x+y)+}]^q} \quad (7)$$

$$= \frac{[R_1^{(p+q)+} + a]^y \cdot [R_2^{x+} + q a/y]^q}{[R_1^{p+} - a]^y \cdot [R_2^{(x+y)+} - q a/y]^q}$$

in which

1. $[R_1^{(p+q)+}]$, $[R_1^{p+}]$, $[R_2^{(x+y)+}]$ and $[R_2^{x+}]$

are the concentrations of the corresponding ions at the melt temperature; i. e., at the temperature of equilibrium with the surrounding atmosphere;

2. $[R_1^{(p+q)+}]$, $[R_1^{p+}]$, $[R_2^{(x+y)+}]$ and $[R_2^{x+}]$

are the concentrations of the corresponding ions at room temperature; and

3. a indicates the increase of the concentration of $R_1^{(p+q)+}$ on cooling from the melt temperature to room temperature.

The values of $[R_1^{(p+q)+}]$ and $[R_1^{p+}]$ can be determined by equilibrating the glass with R_1 at the melt temperature. Similarly, one obtains the values of $[R_2^{(x+y)+}]$ and $[R_2^{x+}]$. In order to determine the value of $[R_1^{(p+q)+}]/[R_1^{p+}]$, the glass is equilibrated with R_1 at different temperatures. Then the logarithm of $\frac{[R_1^{(p+q)+}]}{[R_1^{p+}]}$ is plotted versus $1/T$. As $[R_1^{(p+q)+}]/[R_1^{p+}]$ is proportional to the equilibrium constant of reaction (1), we get a linear relation if the heat of activation, H , is constant (van't Hoff Equation). The value of $[R_1^{(p+q)+}]/[R_1^{p+}]$ can also be determined, and, similarly, that of $[R_2^{(x+y)+}]/[R_2^{x+}]$.

This work describes investigations of the mutual interaction between the redox pairs $Mn^{2+}-Mn^{3+}$, $As^{3+}-As^{5+}$, $Mn^{2+}-Mn^{3+}$ and $Ce^{3+}-Ce^{4+}$ in a sodium borate glass with the composition $Na_2O \cdot 4 B_2O_3$. The values determined experimentally will be compared with those calculated from Equation (7).

2. Methods of Investigation

The chemicals used were of the highest purity. A binary $Na_2O \cdot 4 B_2O_3$ glass, produced in a platinum dish by fusing a mixture of Na_2CO_3 and H_3BO_3 , served as the base glass. A series of glasses with different manganese contents was obtained by melting the base glass with potassium permanganate at about 1000 °C in platinum crucible. No attempt was made to equilibrate the glasses with the atmosphere. Then rectangular glass samples (26 x 9 x 4.5 cm) were made by pouring the melt out into forms.

These were tempered. Then their spectral transmissions were determined for 4.5 mm thickness in a spectrophotometer. The Mn^{3+} concentrations were determined chemically (see Section 6), and the Mn^{3+} content was plotted versus the optical density at different wavelengths.

A series of glasses with definite manganese contents was equilibrated with air at different temperatures. That is, the glasses were melted in platinum boats in an electric furnace until the chemically determined Mn^{3+} content no longer changed. The time needed for that was some 8 hours. Then the Mn^{2+} content was determined from the difference between the total content of Mn and the content of Mn^{3+} . The value of

$\log \frac{[\text{Mn}^{3+}]}{[\text{Mn}^{2+}]}$ was determined and plotted versus $1/T$.

Two other series of glasses of the same composition were equilibrated in air in the same way. One contained a certain amount of arsenic (introduced as sodium arsenate), and the other a certain amount of cerium (introduced as cerium sulfate). The contents of As^{3+} and As^{5+} , and that of Ce^{4+} , were chemically determined. The content of Ce^{3+} was likewise determined from the difference between the total content of Ce and the proportion of Ce^{4+} . The value of $\log \frac{[\text{oxidized state}]}{[\text{reduced state}]}$ was plotted versus $1/T$.

In order to determine the mutual interaction between the oxides of manganese and arsenic, a series of glasses with definite manganese content but differing proportions of arsenic was tempered at 1000 °C. Here the spectral transmission was likewise measured on rectangular samples. Then comparison of the optical densities at 500 and 700 μm with those of glasses having known amounts of Mn^{3+} gave the Mn^{3+} contents of these glasses.

Table 1. EFFECT OF THE TEMPERATURE ON THE $Mn^{2+} \rightleftharpoons Mn^{3+}$ EQUILIBRIUM* / 6

Melt Temperature	Total Content of Mn in %	Content of Mn^{3+} in % $\frac{[Mn^{3+}]}{\Sigma Mn \cdot 100}$	$\frac{[Mn^{3+}]}{[Mn^{2+}]}$	$\log \frac{[Mn^{3+}]}{[Mn^{2+}]}$
1100	0,556	4,30	0,045	2,65
1000	0,556	10,80	0,121	1,08
900	0,556	12,82	0,145	1,16
800	0,556	20,74	0,261	1,41
Room Temperature (27°C)	0,556		$1,365 \cdot 10^3$	8,135

1) Manganese content introduced with 1.6% $KMnO_4$.

Table 2. EFFECT OF THE TEMPERATURE ON THE $As^{3+} \rightleftharpoons As^{5+}$ EQUILIBRIUM*

Melt Temperature	Total Content of As in %	Content of As^{5+} in % $\frac{[As^{5+}]}{\Sigma As \cdot 100}$	$\frac{[As^{5+}]}{[As^{3+}]}$	$\log \frac{[As^{5+}]}{[As^{3+}]}$
1200	0,346	64,00	1,78	0,25
1100	0,346	83,34	5,01	0,70
1000	0,346	93,75	15,00	1,18
900	0,346	97,50	39,00	1,59
Room Temperature (27°C)	0,346		$0,546 \cdot 10^{20}$	20,19

*Translator's Note: Commas in numbers indicate decimal points.

A similar method was used to determine the mutual interaction between the oxides of manganese and cerium. Here, we must note that the chemical determination of the Mn^{3+} content of the glass in the presence of another redox element (e. g., As or Ce) after dissolution of the glass in a suitable solvent is not possible, as the amount of Mn^{3+} changes and displaces the equilibrium in the solution.

Table 3. EFFECT OF THE TEMPERATURE ON THE $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$ EQUILIBRIUM*

Melt Temperature	Total Content of Ce in %	Content of Ce^{4+} in % $\left(\frac{\text{Ce}^{4+}}{\Sigma \text{Ce} \cdot 100} \right)$	$\frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$	$\log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$
1100	0,211	28,0	0,390	1,59
1000	0,211	32,7	0,493	1,69
900	0,211	34,5	0,527	1,72
800	0,211	46,1	0,851	1,93
Room Temperature (27°C)	0,211		$1,20 \cdot 10^3$	3,08

*Translator's Note: Commas in numbers indicate decimal points.

3. Results and Discussion

The effect of the temperature on the equilibria of $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$, $\text{As}^{3+} \rightleftharpoons \text{As}^{5+}$ and $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$ in the glass can be seen from Tables 1, 2, and 3, and from Figure 1. The room temperature values (27°C), which are likewise contained in the tables, were calculated from the following equations (see Figure 1) for

a) the $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$ equilibrium:

$$\log \frac{[\text{Mn}^{3+}]}{[\text{Mn}^{2+}]} = 0,3622 \cdot \left(\frac{10^4}{T} \right) - 3,935, \quad (8)$$

b) the $\text{As}^{3+} \rightleftharpoons \text{As}^{5+}$ equilibrium:

$$\log \frac{[\text{As}^{5+}]}{[\text{As}^{3+}]} = 0,7330 \cdot \left(\frac{10^4}{T} \right) - 4,693, \quad (9)$$

c) the $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$ equilibrium:

$$\log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} = 0,1323 \cdot \left(\frac{10^4}{T} \right) - 1,33, \quad (10)$$

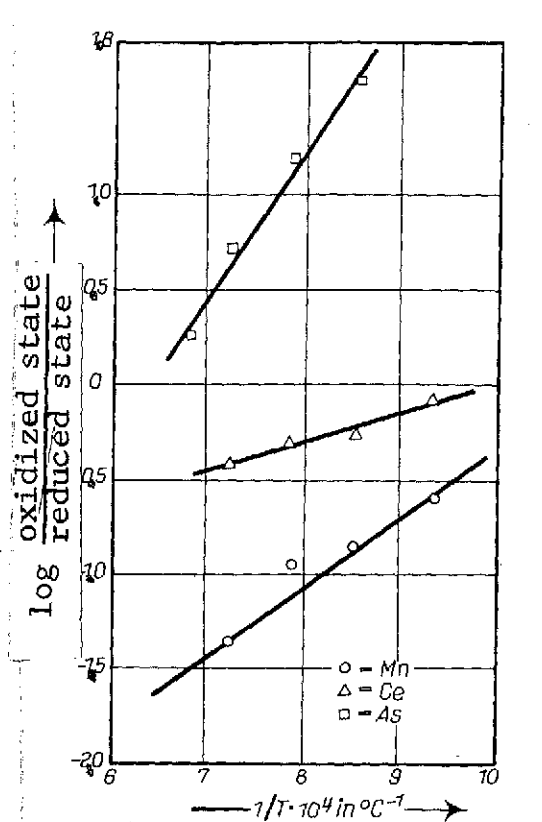


Figure 1. Effect of the temperature on the equilibrium.

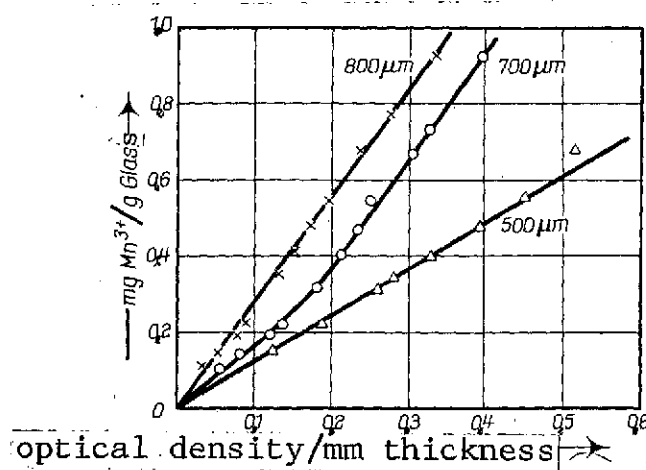


Figure 2. Concentration of Mn^{3+} as a function of the optical density.

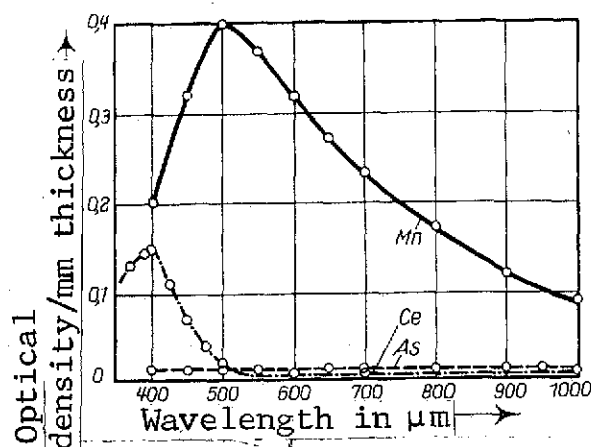


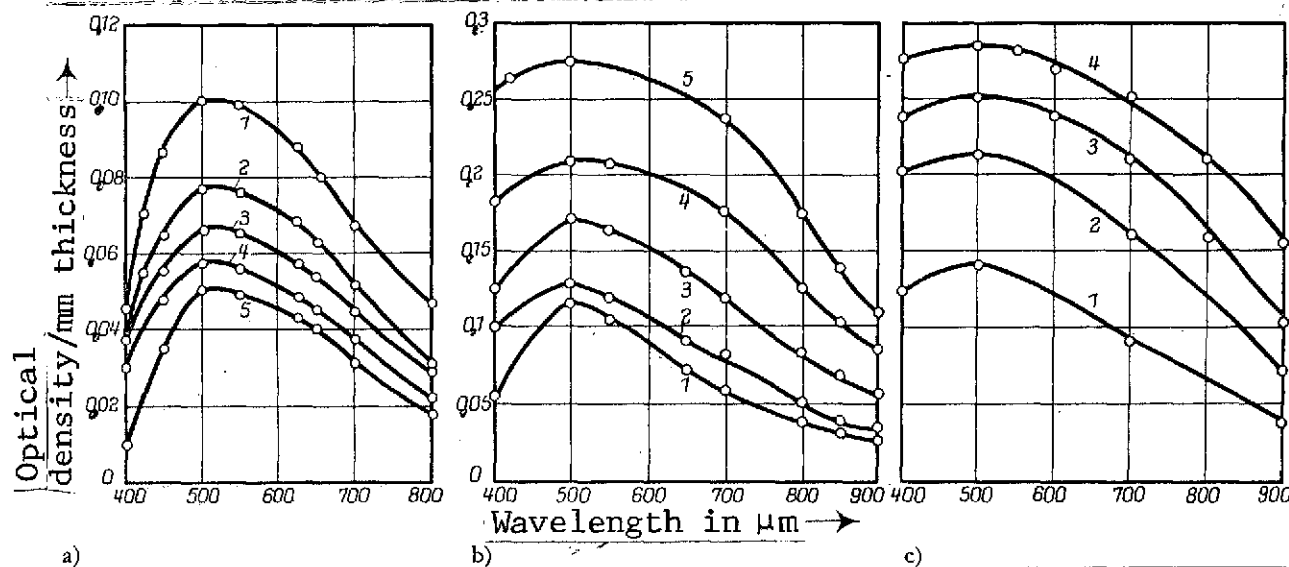
Figure 3. Spectral absorption of glasses containing manganese, cerium and arsenic.

Figure 2 shows the optical densities/mm thickness at 500, 700 and 800 μm as functions of the Mn^{3+} concentration in the glasses. The results indicate that Beer's law is approximately valid.

Figure 3 shows the spectral absorption of the three glasses which contain only manganese, only cerium, or only arsenic.

Figure 4a shows the spectral absorption of glasses with manganese and different amounts of arsenic (equilibrated at 1000°C). Figures 4b and 4c show the absorption in two series of glasses with manganese and different proportions of cerium (equilibrated at 1000°C and 900°C, respectively).

Figure 3 indicates that although Mn^{3+} exhibits an absorption maximum at about 500 μm , the concentration of Mn^{3+} cannot be determined at this wavelength in the presence of cerium which also has considerable absorption at this point. For these



Figures 4 a to c. Spectral absorption of glasses.

a. Glasses containing manganese and arsenic

- 1 = 0,175 % Mn
- 2 = 0,175 % Mn + 0,1 % As
- 3 = 0,175 % Mn + 0,2 % As
- 4 = 0,175 % Mn + 0,3 % As
- 5 = 0,175 % Mn + 0,4 % As;

b. Glasses containing manganese and cerium

- 1 = 0,14 % Mn
- 2 = 0,14 % Mn + 0,1 % Ce
- 3 = 0,14 % Mn + 0,2 % Ce
- 4 = 0,14 % Mn + 0,3 % Ce
- 5 = 0,14 % Mn + 0,4 % Ce;

c. Glasses containing manganese and cerium

- 1 = 0,14 % Mn
- 2 = 0,14 % Mn + 0,1 % Ce
- 3 = 0,14 % Mn + 0,2 % Ce
- 4 = 0,14 % Mn + 0,3 % Ce;

All glasses equilibrated at 1000°C.

All glasses equilibrated at 900°C.

glasses, then, the Mn^{3+} content was determined by comparison of the optical densities at $700 \mu\text{m}$ according to Figure 2. Arsenic, on the other hand, shows no absorption in the visible region. The Mn^{3+} concentration in glasses containing manganese and arsenic could, therefore, be determined by comparison of the optical densities at 500 and $700 \mu\text{m}$. All the results are contained in Tables 4 and 5.

This shows that the addition of arsenic reduces the Mn^{3+} concentration in the glass, while the addition of cerium increases. Similar results were also found by Turner and Weyl [3], Bloch and Sharp [4] and others.

4. Calculation of the Interaction Between Two Redox Oxides

For glasses with manganese and arsenic, we may write Equation (7) as

$$\frac{(K_2)^2}{(K_4)} = \frac{[\text{Mn}_r^{3+}]^2 [\text{As}_r^{3+}]}{[\text{Mn}_r^{2+}]^2 [\text{As}_r^{5+}]} = \frac{[\text{Mn}_m^{3+} + a]^2 [\text{As}_m^{3+} + a/2]}{[\text{Mn}_m^{2+} - a]^2 [\text{As}_m^{5+} - a/2]} \quad (11)$$

where K_2 is the equilibrium constant for the reaction $[\text{Mn}^{2+}] + 1/4 \text{O}_2 \rightleftharpoons \text{Mn}^{3+} + \frac{1}{2} \text{O}^{2-}$ and K_4 is the equilibrium constant for the reaction $[\text{As}^{3+}] + \frac{1}{2} \text{O}_2 \rightleftharpoons [\text{As}^{5+}] + \text{O}^{2-}$ at room temperature, if the indices r and m stand for room temperature and melt temperature.

With

$$[\text{Mn}_r^{3+}]/[\text{Mn}_r^{2+}] = 1,365 \cdot 10^8 \quad (\text{according to Equation (8)})$$

and

$$[\text{As}_r^{5+}]/[\text{As}_r^{3+}] = 0,546 \cdot 10^{20} \quad (\text{according to Equation (9)})$$

we get

$$\frac{(K_2)^2}{(K_4)} = \frac{(1,365 \cdot 10^8)^2}{0,546 \cdot 10^{20}} = 3,42 \cdot 10^{-4} \quad (e)$$

The value $\frac{[Mn_m^{3+}]}{[Mn_m^{2+}]} = 0,08$ can be taken from Figure 1 at 1000°C. Then, for a glass with 0.175% Mn, i. e., $3.164 \cdot 10^{-5}$ moles of Mn/g glass, we get the corresponding concentrations:

$$[Mn_m^{3+}] = 2,34 \cdot 10^{-6} \text{ Mol/g Glass}$$

and

$$[Mn_m^{2+}] = 2,93 \cdot 10^{-5} \text{ Mol/g Glass}$$

For

$$[As_m^{5+}]/[As_m^{3+}] = 12$$

(taken from Figure 1 at 1000°C) and a glass with 0.1% As, i. e., $1.333 \cdot 10^{-5}$ moles As/g glass, we find the concentrations:

$$[As_m^{5+}] = 1,23 \cdot 10^{-5} \text{ Mol/g Glass}$$

and

$$[As_m^{3+}] = 0,103 \cdot 10^{-5} \text{ Mol/g Glass}$$

From this we get

$$\frac{(K_1)^2}{(K_3)} = \frac{(0,08)^2}{12} = 5,33 \cdot 10^{-4},$$

and it follows that

$$\frac{(K_1)^2}{(K_3)} > \frac{(K_2)^2}{(K_4)},$$

That is, the Mn^{3+} concentration should decrease on cooling.

After inserting the values for $[Mn_m^{3+}]$, $[Mn_m^{2+}]$, $[As_m^{5+}]$ and $[As_m^{3+}]$ in Equation (1) we get, approximately,

$$q = -0,28 \cdot 10^{-6}$$

That is, the Mn^{3+} concentration decreases by $0.28 \cdot 10^{-6}$ moles/g glass on cooling to room temperature, to

$$[Mn_r^{3+}] = 2,06 \cdot 10^{-6} \text{ Mol/g Glass} = 0,113 \text{ mg/g Glass}$$

The a values for other arsenic concentrations in the glass were calculated similarly, and the corresponding $[Mn_r^{3+}]$ values were obtained. These values were compared in Table 4 with those determined experimentally.

For glasses with manganese and cerium, Equation (7) may be rewritten in the form

$$\frac{K_2}{K_4} = \frac{[Mn_r^{3+}]}{[Mn_r^{2+}]} \cdot \frac{[Ce_r^{3+}]}{[Ce_r^{4+}]} = \frac{[Mn_m^{3+} + a]}{[Mn_m^{2+} - a]} \cdot \frac{[Ce_m^{3+} - a]}{[Ce_m^{4+} + a]} \quad (12)$$

from which we can calculate a and $[Mn_r^{3+}]$ for various cerium concentrations, as just described. Table 5 contains the calculated and measured values.

Tables 4 and 5 show quite good agreement between the calculated and experimental values. The differences can perhaps be ascribed to the fact that the calculation was done with the assumption of a constant ΔH to room temperature. It is not improbable that ΔH can change over such a wide temperature range. Further, it was tacitly assumed that the activities of the ions are identical, or at least proportional, to the concentrations. This assumption, too, must not really be correct.

Table 4. EFFECT OF ARSENIC ON THE $Mn^{2+} \rightleftharpoons Mn^{3+}$ EQUILIBRIUM*

Melt Temperature °C	Total Content of Mn in the glass in % (2)	Arsenic Content in the glass in %	Optical density per mm thickness at		Mn^{3+} content in mg/g of glass, experimental from comparison of the optical densities at		Calculated
			500 μm	700 μm	500 μm	700 μm	
1000	0,175	—	0,100	0,067	0,120	0,115	0,120
		0,1	0,076	0,052	0,092	0,090	0,113
		0,2	0,066	0,045	0,082	0,080	0,110
		0,3	0,057	0,038	0,070	0,070	0,108
		0,4	0,050	0,031	0,062	0,055	0,107

(2) Manganese content introduced with 0.5% $KMnO_4$.Table 5. EFFECT OF CERIUM ON THE $Mn^{2+} \rightleftharpoons Mn^{3+}$ EQUILIBRIUM*

Melt Temperature °C	Total Content of Mn in % (3)	Cerium content in glass in %	Optical density per mm thickness at 700 μm		Mn^{3+} content in mg/g glass, experimentally from comparison of optical densities at 700 μm		Calculated
1000	0,14	—	0,058	0,10	0,104		
		0,1	0,080	0,14	0,220		
		0,2	0,118	0,20	0,350		
		0,3	0,175	0,31	0,473		
		0,4	0,236	0,47	0,611		
900	0,14	—	0,09	0,15	0,165		
		0,1	0,16	0,28	0,313		
		0,2	0,21	0,40	0,462		
		0,3	0,25	0,52	0,614		

(3) Manganese content introduced with 0.4% $KMnO_4$.

*Translator's Note: Commas in numbers indicate decimal points.

5. References

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6. Appendix
Chemical Estimation of Mn^{3+} , Ce^{4+} , As^{3+} and As^{5+}

Determination of Mn^{3+} : The glass was dissolved, in the absence of air, in the presence of a certain amount of Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) and sulfuric acid ($\sim 2N$). Mn^{3+} reacts with Fe^{2+} , forming Fe^{3+} . The excess of Fe^{2+} ions in the solution is determined by titration with standard potassium dichromate, with N-phenylanthranilic acid as the indicator.

Determination of Ce^{4+} : The same method is used here as for Mn^{3+} . The glass was dissolved by gentle boiling in dilute H_2SO_4 , with air excluded, in the presence of Fe^{2+} ions (solution of Mohr's salt). The excess of Fe^{2+} is titrated with potassium dichromate.

Determination of As^{3+} and As^{5+} : The glass was dissolved in dilute HCl with air excluded. The solution is diluted to a certain volume. As^{3+} is determined in an aliquot volume of the solution by titration with standard iodine solution at $pH = 7$. As^{5+} is determined by addition of KI to another aliquot volume of the solution (acidified to $4N$ with HCl) and the iodine liberated is titrated with standard $Na_2S_2O_3$ solution.

Translated for National Aeronautics and Space Administration under contract No. NASw 2483, by SCITRAN, P. O. Box 5456, Santa Barbara, California, 93108.